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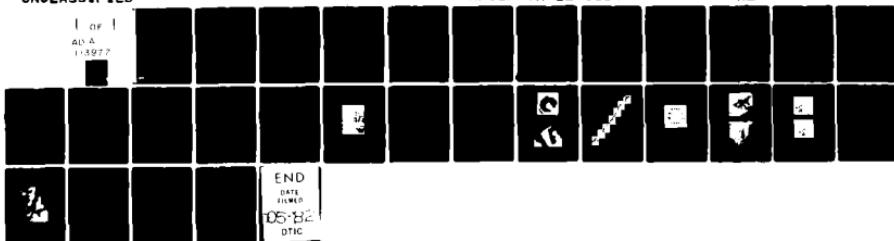
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SILICON NITRIDE JOINING

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Annual Report

February 8, 1982

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Prepared for:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this program is to investigate joining of ceramics through reactions between oxynitride melts and silicon nitride. The basis of the approach is to use joining materials that duplicate the composition of intergranular phases that exist in different types of hot-pressed or sintered Si_3N_4. A method has been devised to calculate average intergranular compositions from bulk analysis of Si_3N_4. Calculated compositions are similar to those determined by analytical electron microscopy. Oxynitrides that simulate the grain boundary phases in NC132 and NCX34 hot-pressed Si_3N_4 were prepared and used in joining experiments. The minimum joint thickness was 15 μ. The integrity of the joints is strongly dependent		

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20 ABSTRACT (Continued)

on the composition of the joining material and on the reaction temperature, but appears independent of the pressure of the nitrogen atmosphere, between 30 and 300 psi. Transmission electron microscopy studies of joined materials suggest that the liquid bonding material reacts with the ceramic surface, dissolving Si_3N_4 and penetrating into the ceramic. At the same time silicon oxynitride laths grow across the interface to form the joint.

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PROFESSIONAL CONTRIBUTION

The Principal Investigator of this program is Dr. Ronald E. Loehman, Senior Materials Scientist, and the Project Supervisor is Dr. David J. Rowcliffe, Program Manager, Ceramics. The transmission electron microscopy studies were performed by Ms. Martha L. Mecartney, Graduate Student, Department of Materials Science, Stanford University, under the supervision of Professor Robert Sinclair.

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INTRODUCTION

A. Background

About two years ago it was discovered that oxynitride glasses can be used to join Si_3N_4 . Preliminary work revealed that the room temperature strengths of some of those joints were greater than any others that had been reported.¹ That observation led to this AFOSR-sponsored project at SRI. The objectives of this program are (1) to optimizate the joining process and (2) to gain a better understanding of the joining mechanisms. The basic idea underlying the approach is that the most advantageous joining composition for a particular type of Si_3N_4 is one that duplicates the composition of its intergranular phase. When Si_3N_4 is sintered or hot-pressed the individual Si_3N_4 grains are joined together by reaction with a liquid formed by melting the additives and impurities. Bulk Si_3N_4 could be joined in an analogous fashion using small amounts of reactive, high temperature liquids that promote dissolution and reprecipitation of the Si_3N_4 at the interface. With proper control, the interface between the joined pieces should resemble a Si_3N_4 grain boundary and would be at least as strong and as durable as the grain boundaries in the bulk ceramic. Work on this program has shown that such joining reactions do occur and that compositions closely matched to those of the particular Si_3N_4 intergranular regions give joints of superior strength.

This report discusses the first year's research, including;

- (1) Selection and synthesis of joining compositions.
- (2) Studies of the effects of time, temperature, reactive liquid composition, and atmosphere on joining.
- (3) Semiquantitative studies of the rates of reaction between Si_3N_4 and the joining compositions.
- (4) Studies of interfacial compositions and microstructures using analytical electron microscopy (AEM).

B. Objectives

The research objectives in the first year were:

- (1) Compare calculated and measured compositions of grain boundary phases in hot pressed silicon nitride.
- (2) Prepare oxide and oxynitride compositions for joining experiments, based on the data from (1).
- (3) Perform joining experiments using the following variables:
 - Melt composition
 - Melt-to-ceramic volume ratio
 - Reaction temperature
 - Reaction atmosphere
- (4) Evaluate bonds by microstructural and microchemical analyses using transmission electron microscopy and x-ray techniques.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Two grades of commercially produced hot-pressed Si_3N_4 , NC132 and NCX34, were used in the joining experiments. Table 1 shows the impurities in the materials, as determined by the manufacturer.

The joining compositions were prepared in several ways. Mixtures containing only oxides were melted in air in platinum crucibles between 1600° to 1650°C using an electric furnace with MoSi_2 elements. Oxynitride compositions were prepared by melting mixtures of the oxides with Si_3N_4 or some other nitrides under N_2 in Mo crucibles using a graphite element furnace that can reach temperatures as high as 2000°C. Oxide mixtures were fritted by pouring the molten charge into water. Both the oxide frits and the oxynitride compositions were ground, acid-treated to remove contaminants from grinding, washed, dried, and sieved to -325 mesh. These powders were used for subsequent joining and reactivity experiments. Compositions of powders prepared in this way are given in Table 2.

In the joining experiments a boron nitride (BN) jig was used to support two plates of Si_3N_4 that were separated by the joining compositions so that the plane of the joint was horizontal, as illustrated in Figure 1. This sample configuration produced a simple butt-seal in which there was no pressure on the joint during reaction except for the weight of the upper plate. This arrangement places severe demands on joint quality and it is thus very useful as a screening tool. The assembly was heated under a N_2 atmosphere in a graphite resistance furnace in which the temperature was measured with either a Pt-6% Rh/Pt-30% Rh thermocouple or an optical pyrometer. Ceramic plates resulting from successful joining experiments were diamond sliced into bars approximately 3 x 3 x 75 mm with the plane of the joint at the midline, perpendicular to the long direction of the bar. Some bars were ground longitudinally for testing in a four-point bending fixture on an Instron universal test machine. Other test bars were sliced

Table 1
IMPURITIES IN OF HOT-PRESSED SILICON NITRIDE

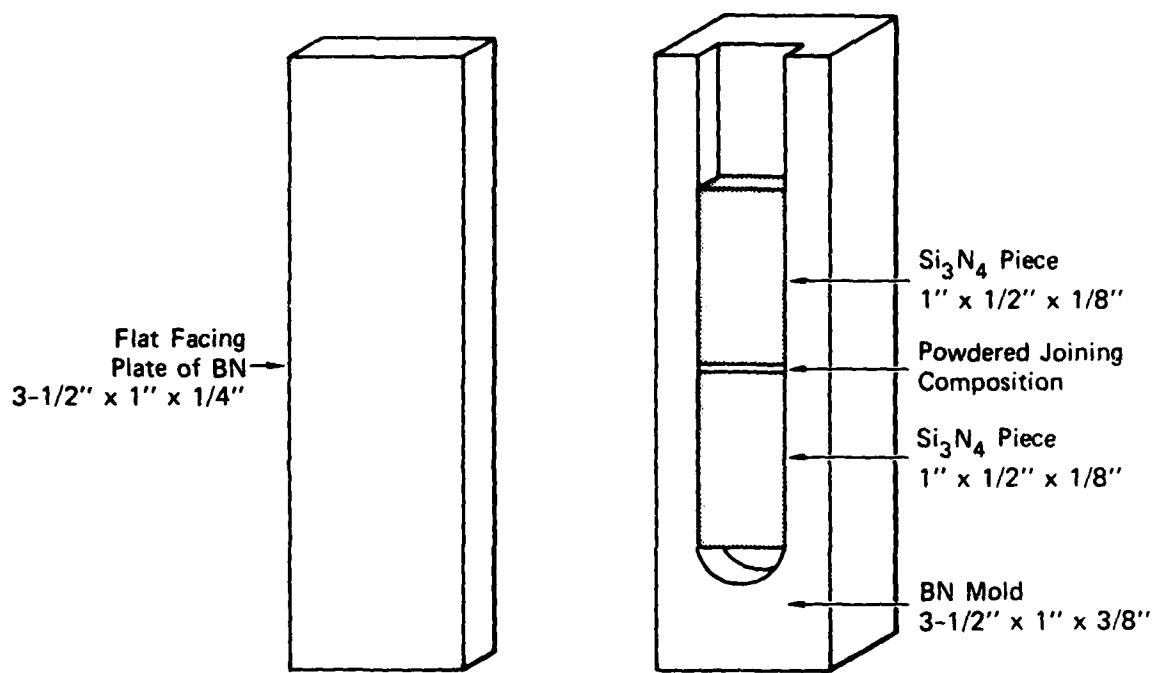
Grade		Analysis in wt%						
	Mg	Y	O	W	Al	Fe	Ca	C
NC132*	powder lot HN-9	0.7	--	1.2	1.7	0.14	0.20	0.02
NC132*	powder lot HN-10	0.8	--	2.6	1.92	0.21	0.20	0.01
NCX34*	powder lot HN-11	--	5.3	1.82	2.1	0.22	0.26	0.01
ND = Not Determined.								

*Norton Co. Worcester, Mass.

Table 2
COMPOSITIONS OF POWDERS PREPARED FOR JOINING EXPERIMENTS

Alloy		Composition in wt%			
	SiO ₂	MgO	Y ₂ O ₃	Al ₂ O ₃	Si ₃ N ₄ *
HN-9M	54.97	35.26	--	9.66	--
HN-9M-5	52.22	33.50	--	9.17	5
HN-9M-10	49.47	31.73	--	8.69	10
HN-9M-15	46.72	29.97	--	8.21	15
SG-14-0	33.9	--	46.0	20.1	--

*CTE Sylvania SN502.



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FIGURE 1 BORON NITRIDE JIG USED IN JOINING TWO PIECES OF Si₃N₄

The two pieces of BN are wrapped with molybdenum wire to hold the jig together.

perpendicular to the joint to produce specimens that were subsequently thinned for analytical electron microscopy (AEM) examination.

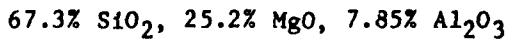
Thin foils for electron microscopy prepared as follows. Slices 0.5 mm thick were cut with a diamond saw perpendicular to the joint so that the thinned specimens contained portions of the Si_3N_4 -glass interface. The slices were surface ground to 100 μm , cut to be 3 mm in diameter, then polished with successively finer grades of diamond paste until a smooth surface was obtained with the last 1- μm grade paste. After being mounted on copper grids, the specimens were ion-milled with argon ions until a hole formed in the specimen. Regions around the hole were thin enough (500-1000 Å) to be electron transparent. The specimens were then coated with a thin layer of amorphous carbon to prevent the specimens from charging under the electron beam. The thinned specimens were examined using a Philips EM400 transmission electron microscope (TEM) equipped with an EDAX 411 unit for energy dispersive analysis of X-rays.

RESULTS AND DISCUSSION

Selection of Joining Compositions

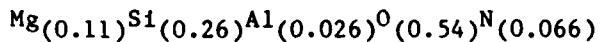
One approach to determining Si_3N_4 intergranular phase compositions is by analytical electron microscopy (AEM), which uses energy dispersive spectroscopy (EDS) and electron energy loss spectrometry (EELS). AEM provides analysis from specific microstructural regions and can therefore be used to examine local variations in composition and to relate compositions with specific microstructural regions. Although AEM is a very powerful method, such analyses require special equipment and are time-consuming because of the necessity to produce thin, electron-transparent specimens. A complementary method is to calculate an average intergranular composition from bulk Si_3N_4 analyses using knowledge of oxynitride glasses and of Si_3N_4 second phase interactions. The calculations are more efficient for determining joining compositions for initial screening studies. Both approaches were used during this project, and the compositions of intergranular phases measured by AEM compare well with calculated compositions.

The calculation of the average composition of the intergranular phase in NC132 was made as follows. Considering the analysis of HN-10 powder, shown in Table 1, it is assumed that all the oxygen is combined with Al, Mg, and Si, ignoring the Ca to a first approximation because of the small amount that is present. (Previous work² showed that Fe and W were combined with carbon or silicon as carbides and silicides.) The composition of the oxide second phase is therefore:



Inspection of the Al_2O_3 - MgO - SiO_2 phase diagram,³ Figure 2, shows that this composition melts at about 1550°C. Other work⁴ in which an oxide glass of similar composition was reacted with Si_3N_4 at 1650°C revealed that about 15 wt% of Si_3N_4 remained in the glass that formed when the melt was

cooled. If that quantity of Si_3N_4 is included in the $\text{Al}_2\text{O}_3\text{-MgO-SiO}_2$ composition calculated above, then the composition of the second phase, expressed as atomic fractions, is:



This is near oxynitride glass compositions⁵ that have glass transition temperatures around 850°C, thermal expansion coefficients of 4.7×10^{-6} $^{\circ}\text{C}^{-1}$, and densities of 2.6 g/cm³. The calculated 6.2 wt% second phase in the hot-pressed ceramic (again ignoring the Fe, W, and Ca) amounts to about 7.5 vol%.

In a similar manner, an intergranular phase composition for any sort of Si_3N_4 can be calculated, provided that a bulk analysis is available. The calculated compositions of the intergranular phases in NC132 made from powder lots HN-9 and HN-10 are indicated in Figure 2. The range of compositions of NC132 necessarily means that the composition of the grain boundary phase is also variable. Local variations in the composition of grain boundary phases can also be expected as a result of failure to reach equilibrium during processing. Such variations have been reported by Clark et al.⁶ who determined a range of compositions for intergranular phases in hot-pressed Si_3N_4 using AEM techniques. The first AEM studies on joined specimens confirm that the Si, Al, and Mg in the glassy phases are in the predicted ratios. Thus the compositions of the joining materials listed in Table 2 reflect the calculated and observed compositions of grain boundary phases in hot-pressed Si_3N_4 . The base HN-9M composition for joining NC132 was selected to lie in the composition range between HN-9 and HN-10. Since the amount of Si_3N_4 that can dissolve in glass increases as the amount of SiO_2 decreases⁵ the composition for HN-9M was chosen to minimize the SiO_2 content and have a melting point around 1550°C, as shown in Figure 2.

Optimization Studies

Much of the first year's work concentrated on understanding how variations in different joining parameters affect the quality of the joint. Specific topics studied were:

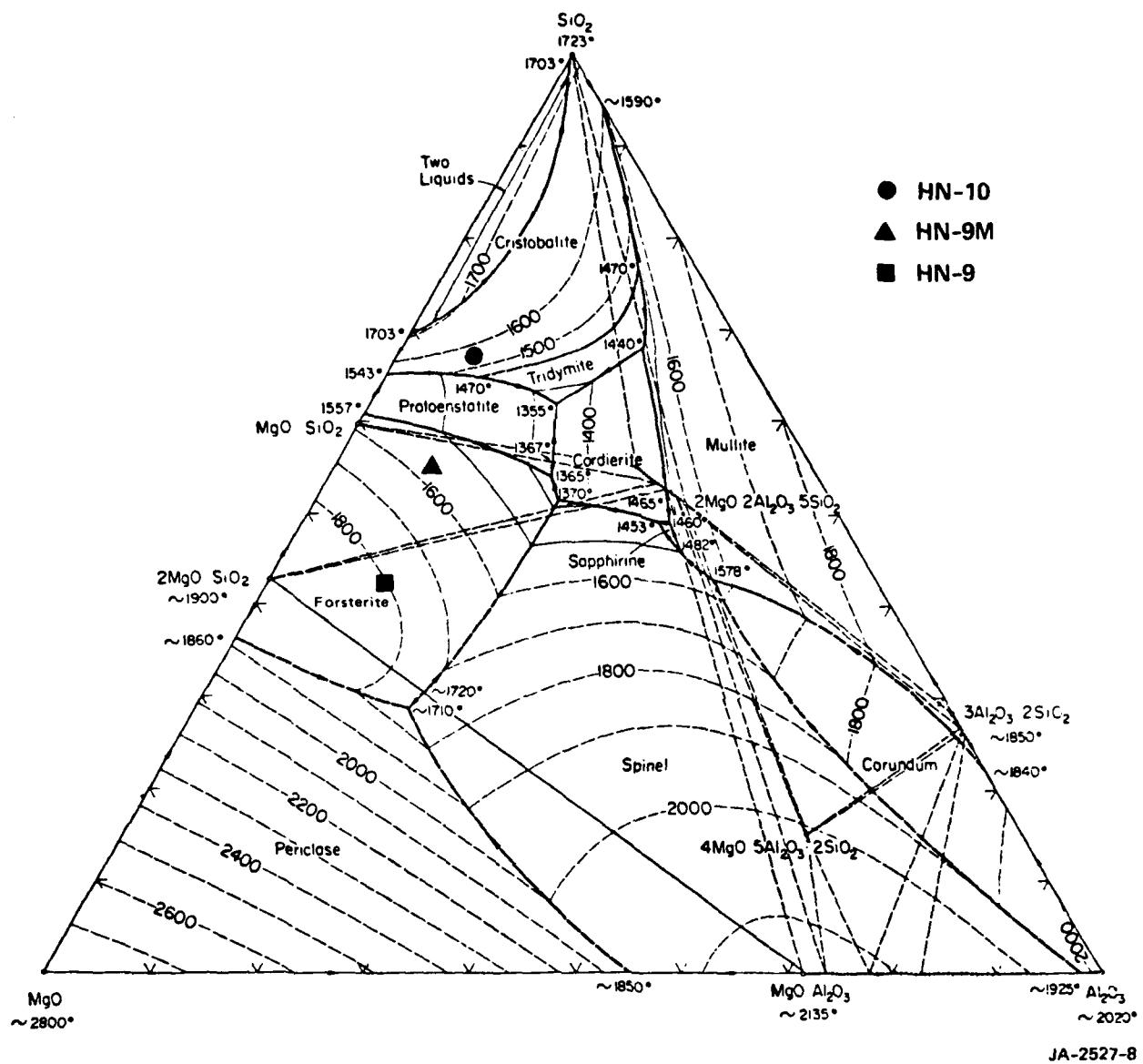


FIGURE 2 MgO-Al₂O₃-SiO₂ PHASE DIAGRAM

HN-9 and HN-10 are calculated grain boundary phases for two powder lots of NC132 Si_3N_4 . HN-9M is the base composition used for joining.

- Range of compositions that can be used to join a particular type of Si_3N_4 .
- Influence of reaction time on microstructure of joints.
- Temperature range for effective joining.
- Influence of quantity of joining glass on structure and properties of joints.

The approach has been to use either NC132 or NCX34 hot-pressed Si_3N_4 as the material to be joined and to vary systematically the joining composition, the amount of the joining material, the reaction temperature, and the time at temperature.

The range of variables studied so far is given in Table 3. Good bonds were strong enough that they could not be broken by hand or during any of the subsequent polishing and grinding procedures; also, the bonds had a thin and continuous joint seam. The minimum thickness achieved so far for the glassy joint region is 15 μm . Figure 3 shows a micrograph of such a joint. As shown in Table 3, most variables significantly affected the joint quality, with the exception of N_2 pressure, where a high pressure of 300 psi N_2 did not improve the joining over a lower pressure of 30 psi.

Si_3N_4 could be successfully joined with a Y-containing glass at temperatures as high as 1700°C, but that temperature was too high for the Mg-containing HN-9M glass, which vaporized and disappeared. Bonding did not occur below the liquidus of each joining composition (~ 1550°C). Near such low temperatures the kinetics of the joining process are very slow and times greater than 30 minutes were required for good joining. Glass compositions with more than 5% Si_3N_4 tended to froth and wet the bulk pieces of NC132 irregularly.

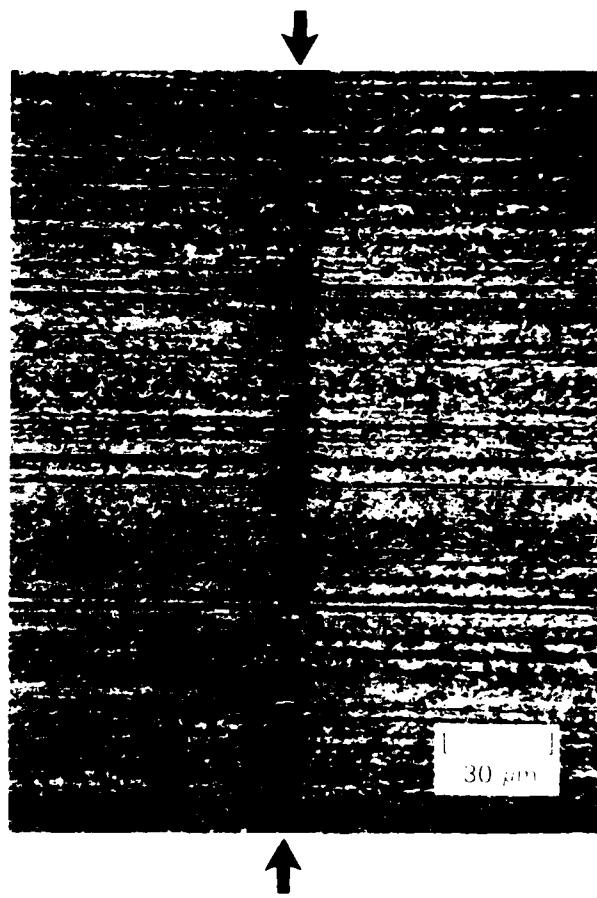
Reactions Between Si_3N_4 and Joining Compositions

At the beginning of a joining reaction the composition at the interface between the bulk Si_3N_4 and the liquid is different from what it eventually becomes once the liquid approaches equilibrium with the ceramic. Specifically, at the interface, the volume fraction of liquid (and hence the oxygen activity) is greater than that of the solid

Table 3

 Si_3N_4 JOINING--OPTIMIZATION EXPERIMENTS

Used	Si_3N_4 Joining Composition	Temp. (°C)	Time (hr)	Nitrogen		Result
				Pressure (psi)		
NC132	HN-9M	1700	1	300		Glass gone, no joining
NC132	HN-9M	1650	3/4	300		Good bond
NC132	HN-9M	1650	1	30		Good bond
NC132	HN-9M	1750	1	30		Glass gone, no joining
NC132	HN-9M	1550	1	30		Good bond
NC132	HN-9M	1575	1/6	30		Incomplete melting
NC132	HN-9M	1575	1/2	30		Good bond
NC132	HN-9M-15	1655	1	30		Frothy joint
NC132	HN-9M-10	1725	1	30		No joining
NC132	HN-9M-5	1620	1	30		Good bond
NCX34	SG14-0	1720	1	30		Good bond



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FIGURE 3 NC132 Si_3N_4 JOINED WITH HN-9M GLASS
Surface ground to a 325 grit finish.
Arrows indicate the joint region.

Si_3N_4 . To model this early stage reaction, 25-g samples consisting of powdered HN-9M glass and GTE Sylvania SN 502 or SN 402 Si_3N_4 were mixed in varying proportions and heated. The samples were reacted in Mo crucibles under N_2 in a graphite-element furnace for set times, after which they were rapidly cooled. A slice of each specimen was examined by X-ray diffraction analysis under conditions that allowed a semiquantitative estimate of the relative proportions of the various crystalline phases that were present. Table 4 lists the results of some of the experiments. The most significant result is that for Si_3N_4 concentrations less than 15 wt%, the reacted mixture is mostly glassy, even for the longer heating times. The tendency for glass formation is less for SN 502 Si_3N_4 (about 60% α -phase) than for SN 402 (amorphous). The quantity of crystalline phases also is greater for larger amounts of Si_3N_4 ; e.g., for a 20:80 glass: Si_3N_4 ratio, the material appears mostly crystalline. The phases in the crystallizing mixtures eventually are those predicted from phase equilibrium data, but at shorter heating times nonequilibrium phases form and disappear.

The implication of these results for joining is that during initial reaction a glassy bond will be formed, but with longer heating times more Si_3N_4 will react to produce crystalline phases.

Analytical Electron Microscopy

Specimens for AEM examination were prepared from NC132 Si_3N_4 joined with HN-9M glass by heating for 60 minutes at 1650°C. Figure 4 is a low-magnification micrograph of a thinned specimen in which the arrows indicate the position of the original joint. Figure 5 is a higher magnification micrograph of the region at the joint shown by the lower arrow in Figure 4. Figure 6 is a composite micrograph of the glass- Si_3N_4 bond indicated by the arrow at point A in Figure 5. The upper part of the composite is mostly in the glassy portion of the joint. Moving down the interface from upper right to lower left, the field of view is progressively into the Si_3N_4 side of the interface. In the glassy portion the long, high-aspect-ratio (lath-like) crystallites have been identified by electron diffraction as silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) (Figure 7). The crystallites on the Si_3N_4

Table 4
PHASES PRESENT IN GLASS/Si₃N₄ COMPOSITIONS

Ratio of HN-9M to Si ₃ N ₄ (wt)	Type of Si ₃ N ₄	Temperature (°C)	Time (min)	Phases*
88:12	402 ⁺	1650	10	G
88:12	402	1650	20	G, vw- α
88:12	402	1650	40	G
88:12	502 ⁺⁺	1650	10	G, vw- α
88:12	502	1650	20	G, st-S, m- α , w- β
88:12	502	1650	40	G, w-S, vw- α
85:15	402	1650	10	G, m-S
85:15	402	1650	20	G, m-S, vw- α
85:15	402	1650	40	G, m-S
85:15	502	1650	10	G, m- α , m β , vwS
85:15	502	1650	20	G, st-S, m- α , m- β
85:15	502	1650	40	G, st-S, vw- β
20:80	402	1650	10	st- β , st-S, vw- α
20:80	502	1650	10	st- α , m- β , m-S

* G = glass, S = Si₂N₂O, α = α -Si₃N₄, β = β -Si₃N₄
st = strong, m = medium, w = weak, vw = very weak.

+ 402 = GTE SN402

++ 502 = GTE SN502

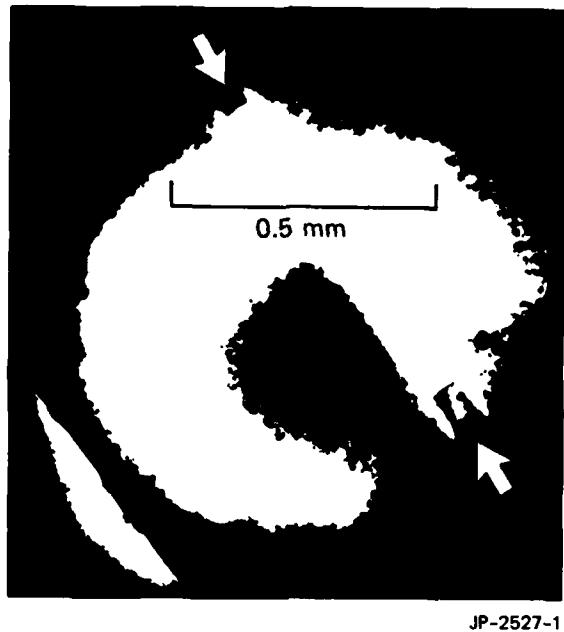


FIGURE 4 THINNED TEM SPECIMEN MADE FROM THE JOINT REGION
The electron transparent regions are around the edges of the hole (white region). Arrows mark the glassy joint.

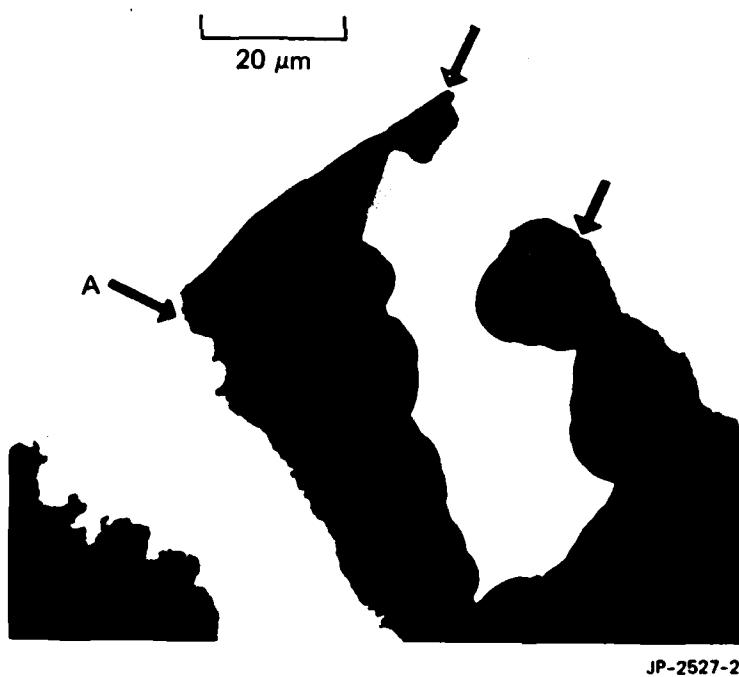
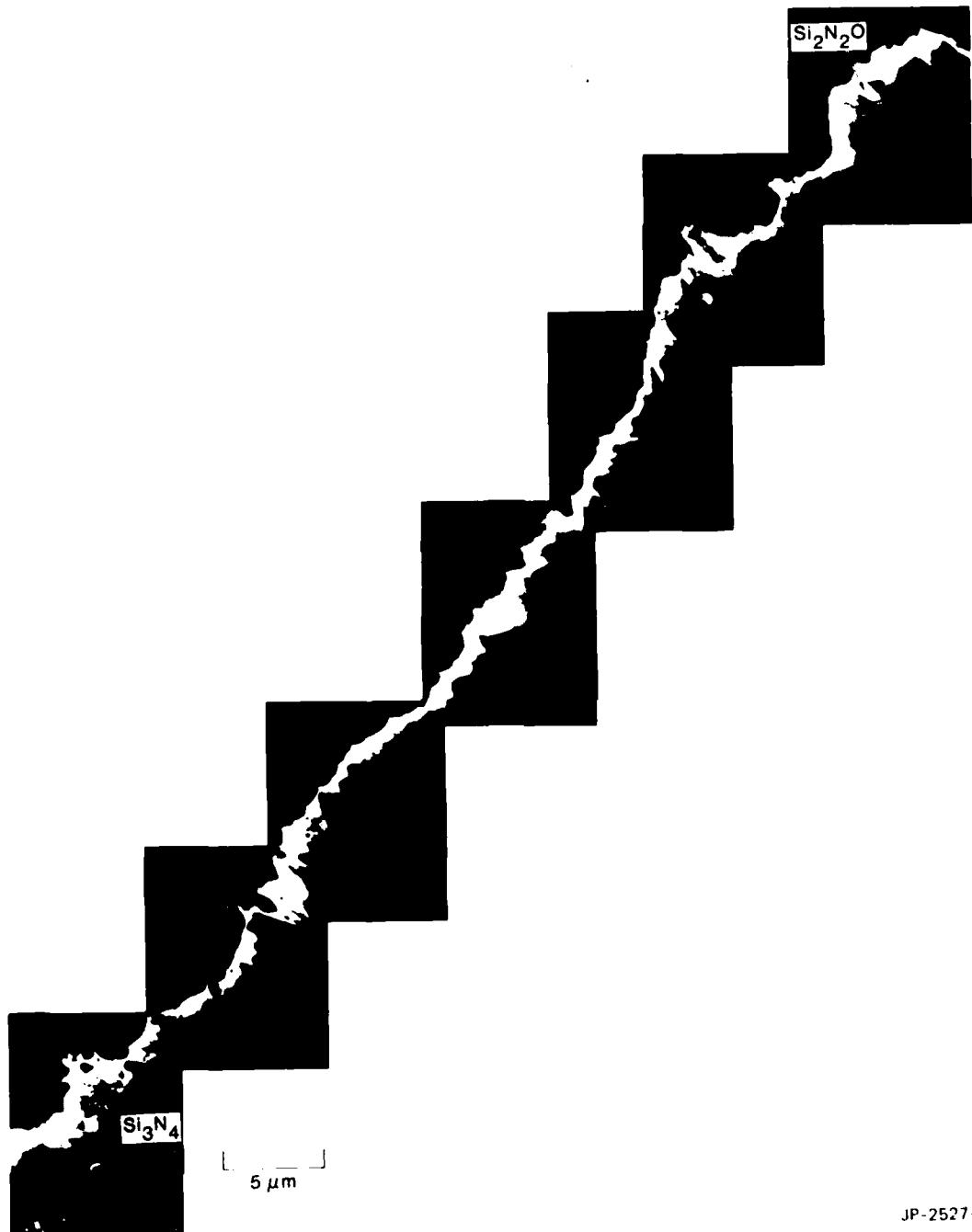


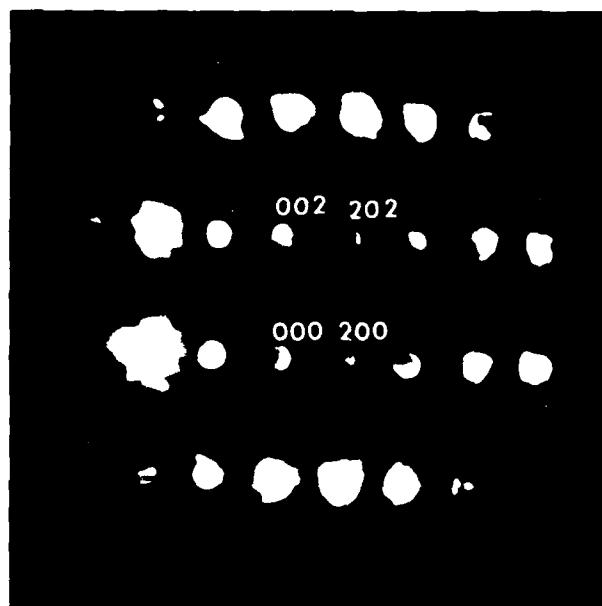
FIGURE 5 GLASSY JOINT ABOUT 45 μm WIDE
The arrows mark places where traces of the original Si_3N_4 -glass interface can be found.



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FIGURE 6 COMPOSITE FROM REGION A OF FIGURE 5

The top right of the micrograph with the lathe-like $\text{Si}_2\text{N}_2\text{O}$ crystallites is at the original Si_3N_4 -glass interface. The lower left is deeper into the Si_3N_4 .



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FIGURE 7 ELECTRON DIFFRACTION PATTERN OF A LATH-LIKE PARTICLE NEAR THE TOP RIGHT OF FIGURE 6

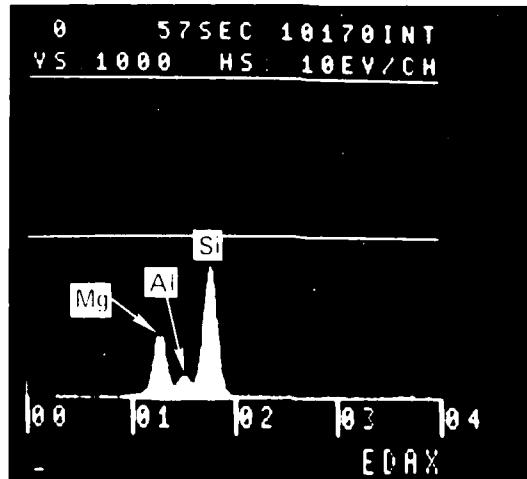
The symmetry of the pattern and the d-spacings calculated from spot separations characterize it as an <020> zone axis for $\text{Si}_2\text{N}_2\text{O}$



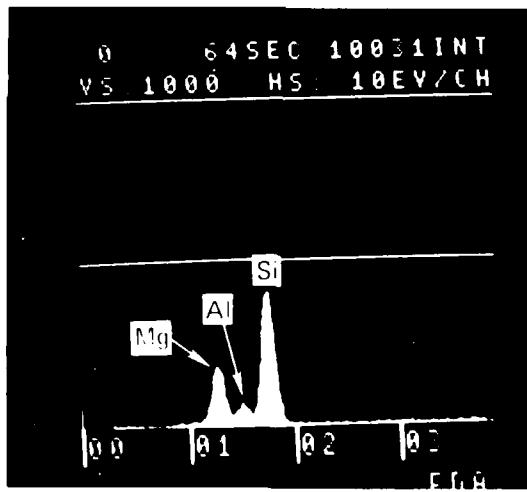
FIGURE 8 AMORPHOUS POCKET (A) IN Si_3N_4 ABOUT 0.25 mm AWAY FROM THE ORIGINAL GLASSY JOINT



FIGURE 9 ANOTHER LARGE GLASSY POCKET (A) IN THE Si_3N_4
Note the many small dark round W particles that are
present in the Si_3N_4 .



(a) GLASSY POCKET IN Si_3N_4 (CORRESPONDS TO FIGURE 9)



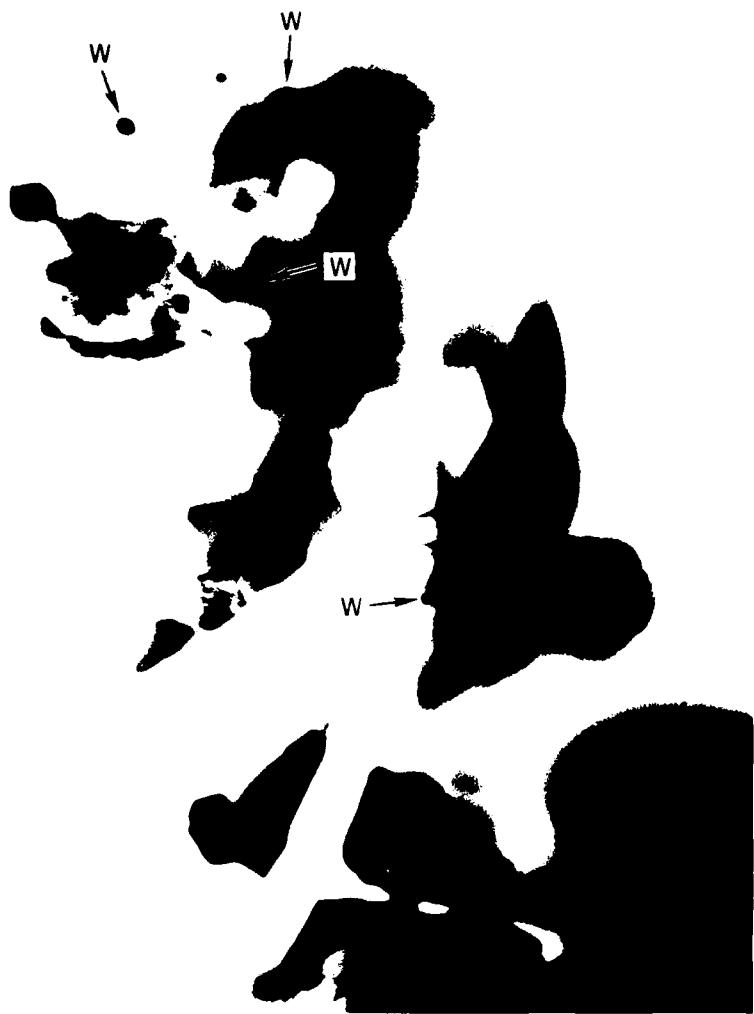
(b) JOINING COMPOSITION (FROM THE CENTER OF THE GLASSY JOINT)

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FIGURE 10 EDS SPECTRA INDICATING SIMILAR MICROCHEMICAL COMPOSITIONS FOR THE AMORPHOUS POCKETS IN THE Si_3N_4 AND THE JOINING GLASS

side of the joint are Si_3N_4 , and it appears that the concentration of glassy phase has been increased by diffusion of glass back into the ceramic. Figures 8 and 9 are views of the Si_3N_4 microstructure about 0.25 mm away from the interface. They also show an increase in the quantity of intergranular amorphous phase. EDS analyses (Figure 10) of the glassy pockets in Figures 8 and 9 and of the glass used in the joint show that the microchemical compositions are the same, at least for the elements detectable by EDS (only elements heavier than sodium, which excludes nitrogen or oxygen analysis). These large pockets of amorphous material are probably due to the glass from the joint penetrating into the ceramic.

Tungsten contaminants from the Si_3N_4 can serve as markers of the original Si_3N_4 -glass interface position before reaction because the tungsten is present initially only in the ceramic. Figure 11 is a micrograph in which the tungsten particles appear as the dark spots distributed to the right of the lath-like $\text{Si}_2\text{N}_2\text{O}$ crystallites. The region to the right is amorphous and it is the remnant of the original joining material. The position of the tungsten in the glass indicates that the glass has penetrated into the ceramic, dissolving it and leaving behind the tungsten. A possible mechanism for the joining process thus emerges: the liquid bonding material reacts with the ceramic surface, dissolving the Si_3N_4 and penetrating into the ceramic. Concurrently, because of local high oxygen activity in the liquid, $\text{Si}_2\text{N}_2\text{O}$ begins to crystallize and grows into the joint. Presumably, if the reaction were continued, Si_3N_4 would appear as an additional phase. The interlocking structure of the $\text{Si}_2\text{N}_2\text{O}$ grains might contribute to the high strengths measured on the early Si_3N_4 joints.¹



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FIGURE 11 TUNGSTEN (W) PARTICLES MARKING THE ORIGINAL
 Si_3N_4 -GLASS INTERFACE

On the right is the joining glass, on the left $\text{Si}_2\text{N}_2\text{O}$
crystallites.

SUMMARY AND RECOMMENDATIONS

From the first year's work, we conclude that the Si_3N_4 joining process has strong potential. Calculated compositions that simulate grain boundary phases of the Si_3N_4 produced successful joining compositions. Techniques for joining two pieces of Si_3N_4 and creating a thin bond were established. Special procedures were developed for thinning specimens for electron microscopy. Analytical electron microscopy provided the information on microstructure and microchemical composition of the bonds and adjoining areas in the Si_3N_4 that suggests a mechanism for the joining process.

We recommend that the following tasks be performed during the next contract year:

- Measure the strength of the bonds by 4-point bend tests at room temperature. Analyze the mode of fracture, including microstructural analyses of the fracture path by SEM or TEM, as appropriate.
- Study the kinetics of dissolution of the Si_3N_4 in the glass and precipitation of secondary phases by examining the position of the tungsten marker particles in relation to the other phases present.
- Measure the depth of penetration of the glass from the joint as a function of time and temperature and the effect on the mechanical properties and fracture path. This will be done using a glass joining composition with a chemical tracer (e.g., La_2O_3) so that the glass penetration can be determined with a microprobe detecting the tracer.
- Heat-treat the joined parts to determine if crystallization can be induced in the joint.
- Perform experiments on joining other types of Si_3N_4 , that is, sintered Si_3N_4 and reaction-bonded Si_3N_4 .
- Measure the thermal expansion coefficient (α) of the glass compositions used for joining to determine their compatibility with Si_3N_4 and change in α with increasing nitrogen content.

- Quantitatively analyze the oxygen and nitrogen content in the various glassy joints and in the grain boundaries and amorphous pockets of the Si_3N_4 . This work will be accomplished using the Electron Energy Loss Spectroscopy system at the Regional Center for Electron Microscopy at Arizona State University.

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